



Comparing Aerosol Properties with Actinic Flux Measurements during TEXAQS 2006

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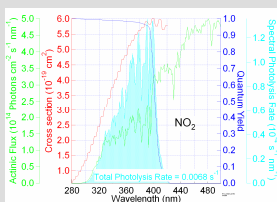
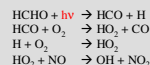
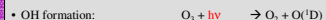
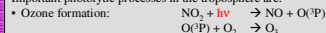
Actinic Flux and Photolysis Rates

Tropospheric chemistry depends critically on photochemistry. Therefore, accurate measurement of all important photolysis rates are required to improve our understanding of air quality issues.

The unit for photolysis is the spectral actinic flux, $J(\lambda)$ [photons $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$], the number of photons reaching the surface of a sphere in the air from all directions per unit time and unit wavelength. In this work, we measured the spectral actinic flux directly by using homogeneous radiation receptors and spectrometers combined in a spectroradiometer on WP-3. Photolysis rates, J , are then calculated for individual photochemical reactions, using the respective absorption cross sections of the molecules, σ , and quantum yields of the reaction, Φ (see equation and figure).

$$J = \int I(\lambda) \times \sigma(\lambda) \times \Phi(\lambda) d\lambda$$

Important photolytic processes in the troposphere are:



Airborne instrumentation on WP-3

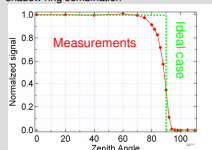
Two spectrometers used for aircraft:

- "Blue" spectrometer: 280-490 nm
- 1340x256 CCD array
- "Red" spectrometer: 460-690 nm
- 1024x256 CCD array

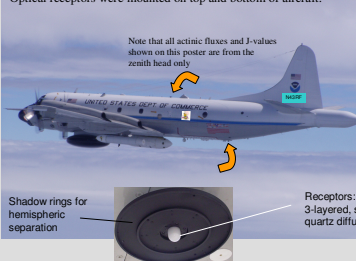
General specifications:

- Pixel resolution = 0.25 nm
- FWHM = 1 nm
- Data averaged to 1 nm
- 1 Hz repetition rate
- Optical fibers from receptors to spectrometers, split to feed both instruments

Zenith angle dependence of receptor – shadow ring combination



Optical receptors were mounted on top and bottom of aircraft:



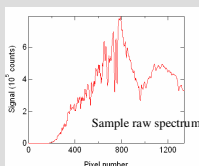
Shadow rings for hemispheric separation

Receptors: 3-layered, sand-blasted quartz diffusers

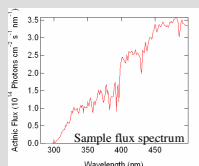
Measurements are corrected for non-ideal zenith angle behavior

Calibration procedures:

- Intensity calibration:
 - Field standard 250-W halogen lamps were calibrated before and after the campaign in the laboratory using NIST-traceable radiation standards.
 - Intensity calibration performed 5 times during campaign.
- Wavelength calibration:
 - Hg atomic emission lamps used in conjunction with sunlight.
 - Atomic emission lines and solar Fraunhofer lines used for wavelength calibration at same time as intensity calibration.
 - All 1-s spectra fitted to Calcium H and K lines (around 400 nm) to compensate for thermal wavelength drift during flights.

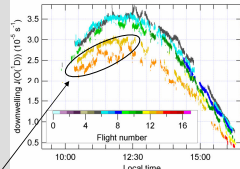


Apply intensity calibration
Apply wavelength calibration

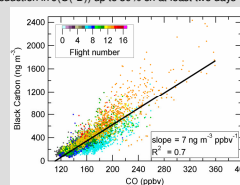


Influence of Black Carbon on Clear-Sky Photolysis Rates and Ozone Concentrations

General picture: clear-sky photolysis rates for nitrogen dioxide ($\text{NO}_2 \rightarrow \text{O}(\text{P}) + \text{NO}$) and ozone ($\text{O}_3 \rightarrow \text{O}(\text{D}) + \text{O}_2$) for all flights in 2006

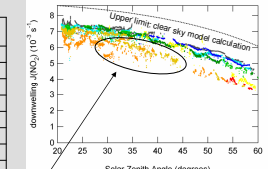


Reduction in $J(\text{O}(\text{D}))$ up to 30% on at least two days



High black carbon signal on days with low photolysis rates (flight numbers 12 and 13), correlated with enhanced CO mixing ratios

Flight number	Flight date
0	8/31
1	9/11
2	9/13
3	9/14
4	9/16
5	9/19
6	9/20
7	9/21
8	9/25
9	9/26
10	9/27
11	9/29
12	10/5
13	10/6
14	10/8
15	10/10
16	10/12
17	10/13



Reduction in $J(\text{NO}_2)$ up to 20% on same days as for $J(\text{O}(\text{D}))$

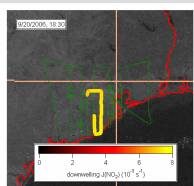
A previous publication (Li et al., JGR 110, D23206, doi: 10.1029/2005JD005898, 2005) calculated regional distribution of black carbon in the Houston area and predicted reductions of 10-30% in $J(\text{O}(\text{D}))$ and $J(\text{NO}_2)$. The study also suggested reductions in ground level ozone by 5-20% because of the reductions in photolysis rates.

Our photolysis rates measurements from TEXAQS 2006 confirm the reduction levels in these photolysis rates.

How do we know it's clear sky?

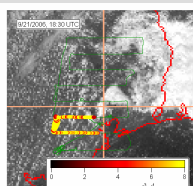
Flight tracks overlaid with satellite images show clouds

Example 1: clear sky on 9/20



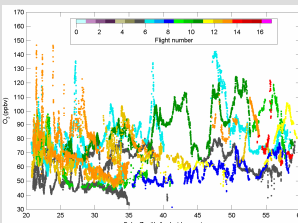
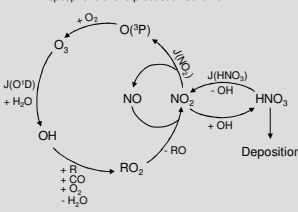
Intermittent clouds (white spots) agree with varying photolysis rates (color-coded flight track)

Example 2: clouds on 9/21



Influence on Ozone Concentrations?

Tropospheric ozone production scheme

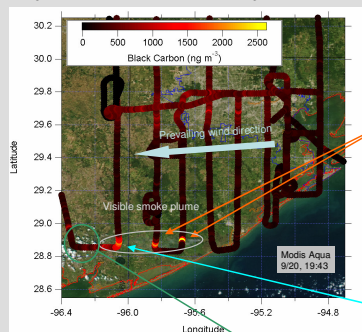


A reduction of ozone mixing ratios correlated with reduced photolysis rates on days with high black carbon loading (flight numbers 12 and 13) could not be seen.

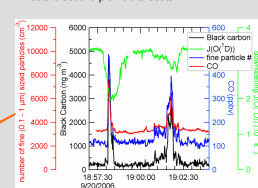
Often, when photolysis rates were reduced by black carbon, ozone precursors (NO , NO_2 , VOC , CO) were enhanced, allowing more efficient ozone production. For example, the correlation plot of black carbon vs. CO (see above) clearly shows a positive correlation.

Change of Actinic flux by Aerosols

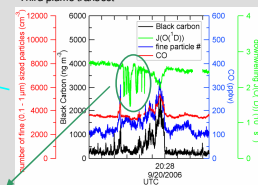
Flight track from 9/20/2006 on Modis satellite image



First and second plume transects

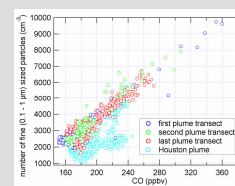


Third plume transect

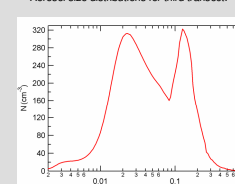


Plume source: local biomass burning

Correlation of fine particle number with CO indicates same plume source for all transects

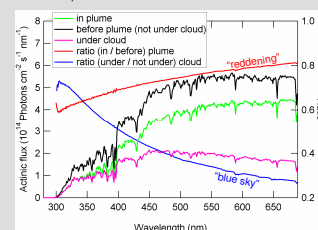


Aerosol size distributions for third transect:



Overhead clouds, produced by plume?

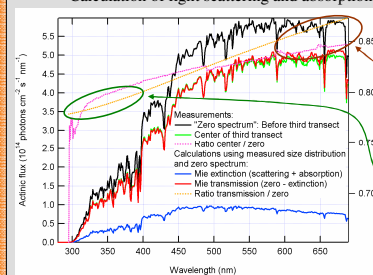
Actinic flux spectra for third transect:



Notice the opposite slopes of the cloud vs. plume ratios:

- Cloud ratio: cloud blocks out significant fraction of direct light, remaining spectrum resembles atmospheric scattered light (blue sky)
- Plume ratio: measurement is conducted within the plume, measured ratio equals transmitted light after light is scattered, blue is more strongly scattered, therefore spectrum shows reddening

Calculation of light scattering and absorption within plume using Mie theory:



Parameters used for Mie calculations:

- Soot refractive index: $m = 1.96 + 0.66i$
- Optical pathlength: 1000 m
- Measured aerosol size distribution
- Downwelling actinic flux spectrum as zero spectrum

Results:

- Good reproduction of measured spectrum in plume
- Calculated spectra ratio close to measured ratio
- Difference in red spectral region: missing larger aerosols?
- Difference at UV wavelengths: additional ozone absorption?